NONTOXIC WATERY SOLUTION AGAINST FREEZING AND CORROSION AND THE REGENERATOR FOR THE UTILIZED ANTIFREEZE

Field of the art

[0001] The present invention is related to the field of cooling internal combustion engines passenger and truck vehicles), and other cooling and heating systems where heat exchangers are used. Precisely, this invention is related to field of fluids – liquids for cooling the operating engine, i.e., to the anti-freezing and anticorrosive agent composition and the antifreeze regeneration agent, primarily glycerin-based, which are absolutely nontoxic.

[0002] The technical problem which is solved is how to obtain an anti-freezing agent useful in open and closed cooling systems, to obtain nontoxic liquid (fluid) for heat exchange, and at the same time to obtain anticorrosive protection in cooling system for all metals, especially for aluminum engines or parts of the engine, i.e., how to obtain composition that will be used for regeneration and modification of anti-freezing and anti-corrosive agent.

State of the art

[0003] There are known cooling fluids which are used in the cooling systems of internal combustion engines, in open and closed cooling systems, which do not freeze at temperatures from -30°C to -40°C. Most of these fluids are marketed under the name antifreeze.

[0004] Mainly, the compositions are specifically formulated with ethylene glycol or propylene glycol, or with derivates thereof and include additives which inhibit and reduce corrosion of the cooling system. To develop specific cooling agent formulations is important because, with appearance of engines with higher performances, especially heavy-duty diesel engines, there are growing numbers of engine components which are produced from a variety of materials to reduce weight and enhance efficacy. Therefore, specific additives are selected so to provide special advantages, such as providing protection for one or more selected materials. However, these additives are often selected in such a way that their beneficial properties are mutually supplemented. Despite formulating specific cooling agent compositions, advantages that are connected to many additives may be disturbed because many drivers pour hard water in

the cooling system. Hard water may be added either after initial filling of the cooling system or during the service, since drivers themselves, but also workers in relevant services add ordinary water in the cooling system (i.e., they change water that has been lost by evaporation and the like).

[0005] However, in many parts of the world there is no available suitable water for use in cooling systems. Hard water contains minerals, mostly calcium, magnesium and iron salts. These minerals may contribute to loss of efficacy and to reduce lifetime of cooling agent composition. The loss may be especially adverse for heavy-duty diesel engines that may pass over 20,000 kilometers per month. Non-effective cooling agent composition may reduce engine lifetime, clog internal passages in the cooling system, contribute to cylinder liner corrosion and clog water pump.

[0006] The trend toward reducing noxious emission has resulted in some progress in engine emission technology, and that progress may induce change of usual ethylene glycol and/or propylene glycol bases which have been for almost one century the main carrier for engine antifreeze formulations. New engine components, especially devices for exhaust gas recirculation (EGR), result in much bigger thermal stress to the engine cooling agent. Ethylene glycol and propylene glycol oxidation may be drastically accelerated, which results in cooling agent that becomes unacceptable for continued usage, even in such short time intervals as several months. Therefore, manufacture is moving toward engine cooling agents which operate in longer time intervals, i.e., toward agents which are possible to regenerate and/or optionally to modify.

[0007] Because of what is stated but also because of number of other reasons, there is continuous need for improvement of cooling agent compositions and for improved processes of corrosion reduction which are connected with cooling agent compositions. This invention represents such improvement and it provides great number of different advantages.

[0008] Examples of patent literature references relating to antifreeze compositions include

- Patent application EP 1010740 A1 discloses solution which comprises glycerol as a basis, but which comprises only 4 additives;

- Invention from patent application published under number WO 03/040254 A1, as basic basis has alcohol, and parts of patent application which are related to glycerin base also have lesser number of additives;

- Inventions from patent DE 1125407, 569771, 1 125 407 are made from mixture of propylene glycol (i.e., glycol – but it is not said which) and glycerol therefore anti-corrosive protection is not sufficient;

- In patent application published under number WO 02/08354 A1 antifreeze is made with basic base of monoethylene glycol of about 69% with small amount of glycerol, and therefore there have not been accomplished sufficient anti-corrosive protection;

- In patent DE 10163337, antifreeze is made with basic base of monoethylene glycol of about 69% with small amount of glycerol, and therefore there have not been accomplished sufficient anti-corrosive protection;

- In patent number 25-40 251, antifreeze is made with basic base of propylene glycol;

- In patent application 048 430 A1, antifreeze is made with monopropylene glycol and ethylene glycol;

- In patent number U.S. Pat. No. 4,000,079 A, antifreeze is made with glycol and other anti-corrosive protection agents;

- In patent number US 455,248 A, antifreeze is made with glycol;

- In patent application 4,404,113 A, antifreeze is made with basic base of 94% monoethylene glycol, and alcohol glycerol have been used as an inhibitor, with other additives;

- In patent number US 489,391, antifreeze is made by using glycol, i.e., ethylene glycol to 94.74%, but there have not been used enough additives;

- In patent application U.S. Pat. No. 5,387,360 A, antifreeze is made with basic base of ethylene glycol to 92.489%;

- In patent application US 2003/0198847 A1, inhibitor protection is made for more types of basic crude materials which are used for antifreeze preparation, and among them glycerol.

[0009] Disadvantages of the foregoing, as well as many other solutions, are that they are toxic, their lifetime is limited to two years, they have insufficient inhibitory protection, they weaken alkali stocks, and their pH value is too low – about 6.2 to 7.2 (it must be between 9.5 and 11.5 according to ASTM standard). The present inventions meet ASTM standards.

Description of the Invention

[0010] This invention is related to new antifreeze/anti-freezing (and anti-boiling) composition with a non-toxic base in water solution in concentration to 96%. This antifreeze may be used concentrated or diluted with distilled water. It is non-toxic.

[0011] Also described is an anti-corrosive inhibitor in water solution for wasted antifreeze, which can be used on the one hand for antifreeze production and on the other for regeneration and modification of that antifreeze when that antifreeze is wasted.

[0012] Detailed descriptions of both inventions are given below, but their specific compositions will be dependent only of application conditions (type of vehicle, other agents, climatic conditions, etc.). In that sense given compositions are not limiting.

[0013] First, anti-freeze and anti-corrosive composition (antifreeze) will be described. This composition includes distilled (softened) water, non-toxic base (glycerol), and suitable inhibitors. By mixing these ingredients, anti-freezing and anti-corrosive agent for engines is obtained, which is ecologically correct, biodegradable, non-toxic and not harmful for natural resources, does not pollute soil and water, not toxic for humans, fishes, animals and pets, and successfully protects engines (protects system against freezing and corrosion, against forming plaque and foam in the system, and increases the boiling point above 120°C).

[0014] For composition of anti-freeze and anti-corrosive agent, following additives are used as inhibitors:

A) Additives as inhibitors
   1. Glycerol
      - chemical formula $C_3H_8O_3$
      - minimum purity of 98.0% (99.5%)
   2. Water – soften or distilled

3. Benzotriazole – effective inhibitor against corrosion of metals in neutral solution
4. Triethanolamine ($(HOCH_2CH_2)_3N$) – an inhibitor against corrosion of iron and steel
5. Sodium tetraborate
   - chemical formula $Na_2B_4O_7$
   - an inhibitor for several metals, aluminum and their alloys
6. Sodium nitrate
   - chemical formula $NaNO_3$
   - protects several metals
7. Sodium nitrite
   - chemical formula $NaNO_2$
   - necessary concentration depends on corrosion conditions and water content in formulation
8. Sodium sulfite
   - chemical formula $NaSO_3$ (without water) or $NaSO_3 \cdot 7\,H_2O$
   - a good inhibitor for magnesium, aluminum or their alloys in alkali environment or in aqueous solution of glycerol.
9. Potassium sulfate
   - chemical formula K_2SO_4
   - minimum purity of 99%
   - easy solubility in water
   - in this formulation, an inhibitor of aluminum, magnesium and their alloys
10. Sodium chromate
    - chemical formula in acids (Na_2CrO_4)
    - corrosion inhibitor of steel, cast iron, aluminum, copper and zinc in aqueous solution of this formulation
11. Sodium benzoate
    - chemical formula $C_7H_5O_2Na$
    - corrosion inhibitor of steel in water solutions and well preserved pH value and alkalis
12. Calcium cyanamide
    - in this formulation, corrosion inhibitor of steel in watery solutions and solutions of salts

13. Sodium hydroxide
    - suitable for aluminum protection as well as for the preserving of alkali reserve and pH value between 9-11

14. Polycarboxylates which are soluble in aqueous and alcohol solutions such as SOKALAN® CP-12S or CP-10 (BASF). In this formulation, ABC COBLEX's polycarboxylates also are useful.

15. Sodium metaborate
    - chemical formula $NaBO_2$ with application in concentrations of from 0.5 to 5 parts by weight
    - an inhibitor for metals in formulation of nontoxic antifreeze based on glycerol

[0015] Process for obtaining antifreeze involves several phases. First, distilled water preparation is performed (softened to I degree), or totally distilled and free from all minerals and contamination. Mixing is performed with polyvalent alcohol (glycerol) at temperatures of 80-90°C, with continuous agitating until homogenization is completed. Basic base to crude material ratios may be different dependent on what is desired to be designed. Main crude material may be 66:34, 70:30, 80:20, and different ratios are possible. In said ratios it is necessary to leave space for inhibitor (modifier, emulsifier) in quantitative content of 10-20%. After that, heating is continued with the same temperature and agitating until homogenization (unification) of the product completed. To inhibit foaming, silicate oil is added in small concentrations (0.004 to 0.009%). Additionally, high quality and also non-toxic dye is added, i.e., the type used for nutrition or cosmetics. Final product is a light green or light blue liquid. Dye is added because the thus obtained liquid is white and clear.

[0016] In other words, the production process involves the following: the substances-additives in group A are mixed, then, additives from group B are mixed, and finally, additives from group C are mixed. After that, on the same sequence as above, there is mixing of groups, one by one, at a temperature of 80°C and at about 100-200 revolutions per minute.

[0017] The mixed additives are mixed into the basic substance, according to tables and sequence, after the preparation of additives. The relative proportions are as follows: for temperature of -25°C, the additives from "A" in Table A are used with 38% of base (glycerol); for temperature of -35°C, the formulation "B" from Table A is used with 48% of base; for

temperature of -55°C, the formulation "C" from Table A is used with 60% of base; and for the temperature of at least -65°C, the formulation "D" from Table A is used with 88% of base. All these combinations can maintain the temperature from 110°C to 160°C.

[0018] Thus obtained antifreeze is non-toxic, biodegradable and does not pollute the environment. Additionally, this is a very durable (resistant) fluid – it can be used for more than six years or 350,000 km in the cooling system. It is useful for temperatures between from -70°C to +160°C, dependent on concentration (max. 96%). At low temperatures this fluid does not change to solid, but to frail, delicate crystals that do not create pressure on the walls of the engine, pipes and other parts, and during engine ignition those crystals are readily heated and melted without damaging engine and other cooling system structures.

[0019] Following Table A shows different antifreeze composition variants, and therewith particular formulations will be dependent on climate and application conditions, and it is provided for use at temperatures from -15° to -70°C and from +110° to +160°C.

TABLE A

FORMULATION	A	B	C	D
Components in %	(additive content in the formulation)			
A)				
- Distilled water	32.40	24.00	24.00	25.00
- Triethanolamine	0.60	1.00	3.10	3.60
- Polycarboxylate	0.60	1.00	2.60	3.40
- Benzotriazole	0.50	1.50	3.20	4.80
B)				
- Distilled water	55.00	48.00	39.00	33.00
- Sodium tetraborate	0.20	0.40	0.60	0.80
- Sodium nitrate	0.20	0.30	0.40	0.45
- Sodium nitrite	0.15	0.25	0.35	0.45
- Sodium sulfide	0.10	0.25	1.10	1.40
- Potassium sulfide	0.13	0.90	2.20	2.90
- Sodium chromate	0.10	0.20	0.65	1.00
- Sodium benzoate	0.10	0.20	0.35	0.45
- Sodium hydroxide	0.03	0.05	0.08	0.10
C)				
- Distilled water	10.00	20.00	19.00	20.00
- Sodium metaborate	0.20	0.30	0.40	0.80
- Calcium cyanamide	0.20	0.35	0.45	0.90

[0020] As already noted, specific composition will depend on application conditions, agent in which it is used, etc.

[0021] Afterwards, product is packed according to market and manufacturer demands. This product can be used immediately.

[0022] Here follows description of composition of anti-corrosion non-toxic inhibitor water solution, i.e., description of regenerator composition for wasted antifreeze. This composition is inhibitor for above said antifreeze and as such it is ingredient of that antifreeze. At the same time, this inhibitor is designed for use as modifier and regenerator for wasted antifreeze, and it extends antifreeze lifetime and refreshes anti-corrosive protection of wide variety of internal combustion engines and also other engines, heating and cooling systems. This inhibitor is used

in small concentrations (from 8 to 12% by weight) for regeneration and modification of wasted antifreeze in which it is poured, i.e., antifreeze with 10% - 18% of inhibitor.

[0023] The invention provides aqueous concentrated anticorrosive formulation, which is suitable for use as additive for wasted fluid – antifreeze in engine cooling system. This invention enables extension of anti-corrosive protection lifetime for fluid/antifreeze in internal combustion engine cooling system. It has great ability for anti-corrosive protection. This agent may be used as emulsifier and modifier.

[0024] It is very important that it is non-toxic. This inhibitor can be added in small amounts to the wasted antifreeze, relative to total weight of wasted antifreeze. This inhibitor is very potent. It regenerates wasted antifreeze, it is resistant to high boiling temperature, it lowers freezing point, has great ability for heating and cooling system anti-corrosive protection, bring alkaline stocks to satisfactory level and raises pH values. It can be used in any antifreeze, it is made of polycarboxylate, and it is soluble in alcohol, alcohol/water mixture and in water alone. It does not corrode nor damage cooling systems, and it is efficacious in low concentrations.

[0025] Conventional antifreeze solutions weaken due to use. Their lifetime is very limited. In old antifreeze solutions, the pH value decreases and protection against corrosion becomes minimal or ceases.

[0026] Besides the additives indicated for the antifreeze composition, the following additives can be useful in the regenerator composition:

1. Glycerol
   - chemical formula $C_3H_8O_3$
   - minimum purity of 98.0% (99.5%)
2. Water – soften or distilled
3. Benzotriazole – effective inhibitor against corrosion of metals in neutral solution
4. Triethanolamine ($(HOCH_2CH_2)_3N$) a corrosion inhibitor of iron and steel in aqueous solutions.
5. Sodium tetraborate
   - chemical formula $Na_2B_4O_7$
   - an inhibitor for several metals, aluminum and its alloys.

6. Sodium tripolyphosphate
   - protects circulating systems such as heat exchangers from 4° to 99°C. It's effective as an inhibitor over a wide range of pH but not below 6. Not toxic.
7. Sodium nitrate
   - chemical formula $NaNO_3$
   - in formula composition protects several metals
8. Sodium nitrite
   - chemical formula $NaNO_2$
   - necessary concentration depends on conditions of corrosion and water composition in formulation.
9. Sodium sulfite
   - chemical formula Na_2SO_3 (without water) or $NaSO_3 \cdot 7\,H_2O$
   - good corrosion inhibitor for magnesium, aluminum or their alloys in alkali environment or in aqueous solution of glycerol.
10. Potassium sulfate
    - chemical formula K_2SO_4
    - purity of at least 99%
    - easily soluble in water
    - in this formulation inhibitor of aluminum, magnesium or its alloys.
11. Sodium meta-silicate
    - inhibits corrosion of aluminum in aqueous solution of this formulation.
12. Potassium dichromate
    - used for metal protection in contact with antifreeze.
13. Sodium chromate
    - chemical formula in acids ($NaCrO_4$)
    - inhibitor of corrosion of steel, cast iron, aluminum, copper, zinc and brass in aqueous solution of this formulation.
14. Sodium benzoate
    - chemical formula $C_7H_5O_2Na$
    - inhibitor of corrosion of steel in aqueous solutions and maintains pH values and alkalis.
15. Benzolsulfamide
    - chemical formula $C_6H_5SO_2NH_2$

- inhibitor of corrosion of black metals
- in this formulation also of other metals and their alloys

16. Calcium cyanamide
    - in this formulation inhibitor of corrosion of steel in water solutions and salt solutions

17. Sodium hydroxide
    - suitable for aluminum protection as well as for maintaining pH value of 9-11

18. Polycarboxylates which are soluble in water and alcohol solutions such as SOKALAN® CP-12S or CP-10 (BASF). In this formulation, ABC COBLEX's polycarboxylates also are useful.

19. Silicate oil

[0027] Therefore, to maintain pH values between 9.5 and 11, silicates are used which are especially important for aluminum engines for protection of aluminum components in the cooling system and also for maintaining alkalinity of the fluid. The most important component for pH value maintenance is sodium hydroxide, which can be used at 0.5 to 10% by weight in solution.

[0028] Table B shows different variants of anti-corrosive non-toxic inhibitor compositions and regenerator-modifier compositions for wasted antifreeze.

TABLE B

FORMULATION	A	B	C
Components (%)			
A)			
- Glycerol	82.95	75.65	63.55
- Distilled water	5.00	5.00	5.00
- Polycarboxylate	1.0	1.30	1.60
- Benzotriazole	1.0	2.20	4.20
- Triethanolamine	0.80	1.10	1.60
- Sodium metasilicate	0.20	0.40	0.90
- Potassium dichromate	0.30	0.70	1.10
B)			
- Distilled water	5.00	5.00	5.00
- Sodium tetraborate (borax)	0.30	0.45	0.90
- Sodium nitrate	0.35	0.40	0.70
- Sodium nitrite	0.20	0.45	0.60
- Sodium sulfide	0.30	0.90	2.20
- Potassium sulfide	0.25	0.40	1.20
- Sodium tripolyphosphate	0.20	0.60	0.75
- Sodium chromate	0.20	0.45	1.20
- Sodium benzoate	0.30	0.85	1.20
- Sodium hydroxide	0.03	0.05	0.08
C)			
- Benzosulfamide	0.30	0.45	1.00
- Calcium cyanamide	0.45	1.10	1.20
- Silicate (silicate oil)	0.005	0.005	0.005

[0029] Thus obtained regenerator is nontoxic.

[0030] For corrosion inhibition of all engine types, besides said inhibitors, monocarboxylic acids, and polycarboxylates in relatively small concentrations are suitable. Also, azole compounds, including mercaptobenzotriazole, benzotriazole salts, and polytriazole salts can be included. Preferred are nitrate salts, nitrite salts, and mixtures thereof. Also, phosphates may be used which are useful for corrosion inhibition, as is polycarboxylate.

[0031] Improved stable polycarboxylate type is based on polyacrylic acid or polymaleic acid. These polycarboxylates are compatible with other components as in process for obtaining and in subsequent fluid utilization. Examples for polycarboxylates which can be used are those which are produced by BASF under the trade name SOKALAN. These are polycarboxylates which are available as water solutions. This additive generally may be used in formulation from 0.01 to 10%, but it is preferred from 0.01 to about 0.1% (by weight).

[0032] Process for obtaining is conducted in the reactor (container) by heating and cooling to maintain a constant temperature between 80°-90°C. Mixing process after the heating takes about 1 h. This process uses 20-40% distilled (softened) water, 20-30% propylene glycol, 10-20% polyvalent alcohol (glycerol) and other inhibitor components. After that follows cooling and packing according to market needs.

[0033] This regenerator for antifreeze is tested by modified method in 3 X 3 ASTM method and in DIN and by using DIN method. Additionally, standard test method for corrosion in engine coolant in glass vessel is used, with corrosive solution.

BRIEF REVIEW OF ANTIFREEZE AND REGENERATOR FOR WASTED ANTIFREEZE TESTS

a) Antifreeze composition is tested and metal sample purification procedure is conducted according to modified ASTM specification.

[0034] At required temperature, 30-33% of corrosive water is used according to ASTM. All changes are weighted in mg, and they meet the standards.

Table 1

	Allowed (ASTM)	Finding
Copper	5	-0.8
Solder	10	+0.6
Brass	10	-0.6
Iron	5	+0.2
Gray smelting	5	-2.4
Aluminum	10	-5,0

[0035] Findings from ASTM tests from Table 1 meet the standard.

b) Analogous corrosion tests

b1) Corrosion: coupons weight loss (the most mg)

Table 2

	Allowed (ASTM)	Finding
Copper	5	-0.6
Solder	10	+0.1
Brass	10	-0.6
Iron	5	+0.1
Gray smelting	5	-2.3
Aluminum	10	-5.9

[0036] Findings are obtained according to modified ASTM method. Findings meet the standard.

b2) Corrosion: coupons weight loss, the most mg (JUS H.Z8.O56)

Table 3

	Allowed (ASTM)	Finding
Copper	5	+1.9
Solder	10	+1.8
Brass	10	+2.7
Iron	5	+3.4
Gray smelting	5	+3.7
Aluminum	10	+4.0

[0037] Findings are obtained according to analogous method by JUS HZ8.O56 in glass vial with corrosive liquid 30%, and antifreeze 1:1 for temperature -18°C.

[0038] Herein described antifreeze (i.e., anti-freezing and anti-corrosive agent) which is obtained by using regenerator for wasted antifreeze (with inhibitor), and regenerator alone, have been subjected to the following analyses:

1. Examination by University in Novi Sad, Faculty for technical science, laboratory for physical-technical and solar measurements in 1988 and 1989. Findings meet TUB, ASTM and DIN standards.

2. An extreme exploitation test was performed for this antifreeze and regenerator on metallic coupons, according to modified ASTM method and specification. In such a way plates were installed in the cooling systems of General Motors engines: Pontiac 2300 cc and 3100 cc, 1991 models, Chevrolet Corsica 3100 KW and Beretta 2300 cc, 1991 models. Coupons were used in vehicles driven during winter and summer period at external temperatures of -15°C and between +35°-40°C. Between 5,000 and 20,000 km were passed in these tests with normal driving, as in common everyday car driving.

[0039] According to this examination results were obtained as in Table 4 (exploitation method).

Table 4

	Allowed	Finding Corsica	Finding Beretta	Finding Pontiac 2300	Finding Pontiac 3100
Copper	5	-1.2	-1.2	+2.4	+1.9
Solder	10	-2.4	-2.4	-0.5	+1.8
Brass	10	-0.2	-0.2	+0.6	+2.0
Iron	5	+0.6	+0.6	+1.4	+8.6
Gray smelting	5	+3.4	+3.4	+3.6	+6.1
Aluminum	10	+3.7	+3.7	+6.1	+3.6

[0040] Corsica 3100 cc passed 7,000 km; Beretta 2300 cc passed 5,000 km; Pontiac 2300 cc passed 10,000 km; and Pontiac 3100 cc passed 20,000 km. In all the vehicles coupons were installed for 8 months. Coupons were installed in the cooling systems at the highest gravitation pressure. For example, water pump operating pressure was at an average about 1 kPa. Average engine operating temperature was about +110°C. After coupons were removed, coupons were processed according to ASTM standard.

[0041] Findings indicate that this antifreeze is in accordance with high ASTM standard and satisfactory for all the engines in which it is used in their cooling systems, and not only in warranty period, but above 300,000 km and after 6 years of engine exploitation.